

OXIDATION OF THE $[nido-6,9-C_2B_8H_{10}]^{2-}$ ANION – AN ALTERNATIVE SOURCE OF THE 1,6- AND 1,10-DICARBA-*closo*-DECABORANES(10)

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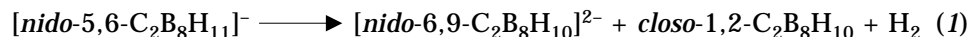
Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday for his major contributions to the area of cluster borane chemistry.

The oxidation of the $[nido-6,9-C_2B_8H_{10}]^{2-}$ (**1**) dianion with $CuCl_2$, is supposed to proceed *via* an unstable *closo*-2,6- $C_2B_8H_{10}$ (**2**) intermediate, which is then rearranged into *closo*-1,6- $C_2B_8H_{10}$ (**3**) (yields 30–35%). The synthesis is accompanied by the formation of the isomeric *closo*-dicarbaboranes 1,10- $C_2B_8H_{10}$ (**4**) and 1,2- $C_2B_8H_{10}$ (**5**) and the whole procedure can be modified to isolate only isomer **4** (yield 35%). Side products from the synthesis consist of a complex and so far unseparable mixture, in which *arachno*-4,6- $C_2B_7H_{13}$, chloro derivatives *closo*- $C_2B_8H_9Cl$, and trimeric compounds of a *closo*-($C_2B_8H_9$)₂- $C_2B_8H_8$ formulation were detected by GLC/MS techniques. These findings point to the involvement of a radical-chain mechanism in the reaction.

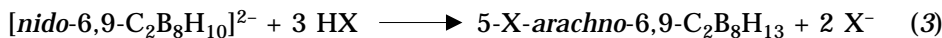
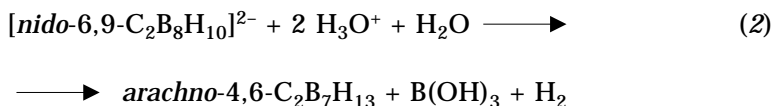
Key words: Boranes; Carboranes; Dicarbaboranes; Ten-vertex *closo*-dicarbaboranes; Radical oxidations; Copper (II) chloride.

One of our groups was the first to report¹ a high-yield synthesis of the $[nido-6,9-C_2B_8H_{10}]^{2-}$ dianion (**1**) *via* thermal disproportionation of the sodium salt of the $[nido-5,6-C_2B_8H_{11}]^-$ anion².

120–200 °C

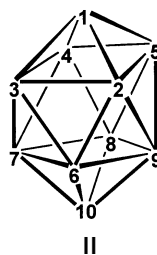
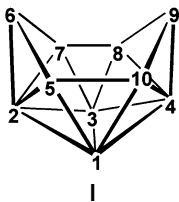


Anion **1** was found to be an excellent source of other dicarbaborane compounds, such as *arachno*-4,6- $C_2B_7H_{13}$ (ref.¹) and 5-substituted halo derivatives of *arachno*-6,9- $C_2B_8H_{14}$ (refs.^{3,4}):



(where X = F, Cl, Br, and I).

Apart from these syntheses, anion **1** was also employed as an excellent starting material for the preparation of a series of variable-structured eleven-vertex metalladecaboranes of the $[1-L_n-1,2,3-MC_2B_8H_{10}]$ type (where L = trialkyl-, alkylaryl-, or trialkoxyphosphines or dialkylsulfides; M = Pt, Ni, and Sn) *via* various metal-incorporation reactions⁵⁻⁹. We wish to report here another example of a simple synthesis based on anion **1** leading to the formation of the isomeric *closo*-dicarbaboranes **3** and **4**. The numbering system for the ten-vertex *nido* and *closo* compounds used in this work is in general structures **I** and **II**, respectively.



EXPERIMENTAL

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver¹⁰ although some operations, such as column chromatography, were carried out in air. The $Na_2[nido-6,9-C_2B_8H_{10}]$ salt was prepared as reported previously¹ and the Aldrich hexane and CH_2Cl_2 were dried over CaH_2 , and freshly distilled before use. Anhydrous $CuCl_2$ was prepared by heating $CuCl_2 \cdot 4 H_2O$ at 200 °C for 6 h *in vacuo*. Column chromatography was performed on silica gel (Silpearl, Kavalier) and the purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil; detection by UV_{254} or diiodine vapour, followed by spraying with 2% aqueous $AgNO_3$). Low-resolution mass spectra were obtained using a MAGNUM GC/MS ion-trap system (Finnigan MAT, U.S.A.) equipped with a heated inlet option (Spectronex AG, Basel,

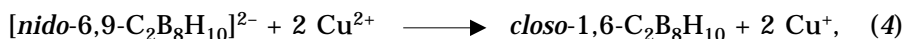
Switzerland). The transfer line was heated at 280 °C and the ion-trap manifold temperature was maintained at 200 °C. The ion trap operated in the EI mode and was tuned using default software settings (Magnum 2.4, Finnigan MAT) to obtain suitable mass calibrations, filament emission current, multiplier voltage, and AGC (Automatic Gain Control) settings. Individual components of the reaction mixture were separated on an on-line Varian 3400 gas chromatograph equipped with a Varian 1075 injector. A DB-5 ms capillary column (JW Scientific, U.S.A., 30 m × 0.25 mm, 0.25 μm film thickness, He (99.96%) carrier gas of velocity 36 cm/s at 60 °C) was used. The GC oven temperature was maintained at 60 °C for 1 min, increased at rate 8 °C/min to 100 °C and then at 15 °C/min to a maximum of 250 °C. The purity of carboranes **3** and **4** was checked by ¹¹B (160.4 MHz) NMR spectroscopy on a Varian XL-500 spectrometer.

Dicarbaboranes *closo*-1,6-C₂B₈H₁₀ (**3**) and 1,10-C₂B₈H₁₀ (**4**)

In a typical experiment, anhydrous CuCl₂ (13.2 g, 100 mmol) was added in portions to a suspension of Na₂[nido-6,9-C₂B₈H₁₀] (**1**) (6.1 g, 50 mmol) in CH₂Cl₂ (100 ml) under vigorous stirring at ambient temperature for 1 h. The mixture was then heated at reflux under stirring for additional 12 h. The mixture was filtered *in vacuo* and the insoluble solid materials washed with two 10 ml portions of CH₂Cl₂. The filtrate was then evaporated *in vacuo* and the residual oily product extracted with ten 10 ml portions of degassed pentane. The combined pentane extracts were evaporated and the residual material was subjected to column chromatography using pentane as the mobile phase. The combined fractions of *R_F* 0.40–0.60 were evaporated and sublimed at ca 50 °C (bath) onto a finger cooled to ca -40 °C to yield typically 1.8–2.1 g (15–17.5 mmol; 30–35%) of a white solid which was identified as carborane **3** by ¹¹B NMR spectroscopy by comparison with the authentic material¹¹. The front fraction of *R_F* ca 0.65–0.80 was evaporated to dryness and sublimed in the same manner to give typically 0.5–1.2 g (2.5–5 mmol; 5–10%) of a mixture consisting of equimolar amounts of compounds **3** and **4**. This mixture was converted quantitatively into the pure isomer **4** by heating in a sealed glass tube at 350 °C for 3 h. Alternatively, the combined fractions of *R_F* ca 0.40–0.80 were evaporated and sublimed at ca 50 °C (bath), and the sublimate was heated at 350 °C in a sealed glass tube for 3 h to give 2.1 g (35%) of compound **4**. In another experiment, the aforementioned CH₂Cl₂ extract was evaporated to dryness and analysed by GLC/MS. The results of the analysis are presented in Table I. Sublimation of this residue at 45 °C (bath) onto a finger cooled to -40 °C gave a white, solid sublimate (2.3 g). According to the GLC/MS analysis, it consisted of carboranes **4** (4.6%), **3** (82.1%) and 4,6-C₂B₇H₁₃ (13.3%) (estimated by GLC peak areas). This mixture can be separated by column chromatography in pentane to isolate typically 1.8 g (30%) of **3** by sublimation in the same manner as outlined above (the sublimate can be also converted into **4** by heating in a sealed glass tube at 350 °C (yield 2.1 g; 35%)). The sublimation residue was then sublimed, maintaining the bath temperature in the range 150–200 °C over a period of 6 h to collect a viscous material (ca 2.5 g). This was identified by GLC/MS analysis as a complex, unseparable compound mixture consisting of chloro derivatives C₂B₈H₉Cl, accompanied by the trimeric *closo*-(C₂B₈H₉)₂-C₂B₈H₈ carboranes.

RESULTS AND DISCUSSION

Treatment of the disodium salt of the $[nido-6,9-C_2B_8H_{10}]^{2-}$ dianion¹ (**1**) with two equivalents of anhydrous $CuCl_2$ for 12 h in refluxing dichloromethane, followed by chromatographical separation of the products in pentane, resulted in the isolation of carborane **3** as the main product in average 30% yields. The prevailing reaction mode, the formation of the *closo*-carborane **3**,



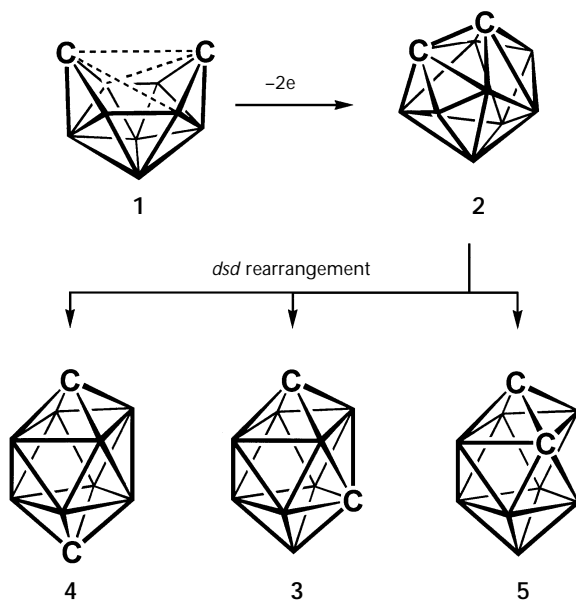
is consistent with a simple two-electron oxidation of **1** as in Eq. (4). In this respect, reaction (4) is a typical *nido* \rightarrow *closo* transformation in the ten-vertex cluster series. Although the mechanisms of this reaction have not been studied in detail, several steps in the reaction sequences may be significant. As outlined in Scheme 1 (simplified structures, the C vertices stand for {CH} units and the unmarked vertices denote {BH} groups), the

TABLE I
Results of the GLC/MS analysis of the reaction mixture

Compound	m/z_{max} , (%)	m/z_{max} , 100%	t_R , min	Rel. peak area, %
$C_2B_7H_9$	110 (55)	108	3.28	1.5
1,10- $C_2B_8H_{10}$	122 (35)	120	3.54	7.2
1,6- $C_2B_8H_{10}$	122 (18)	119	4.59	63.3
$C_2B_8H_9Cl$	158 (10) ^a	154	6.19	2.3
$C_2B_8H_9Cl$	158 (10) ^a	154	6.41	2.2
$C_2B_8H_9Cl$	158 (5) ^a	154	7.40	1.8
$C_2B_8H_9Cl$	158 (5) ^a	154	7.55	1.9
1,2- $C_2B_8H_{10}$	122 (10)	119	8.27	3.8
4,6- $C_2B_7H_{13}$	114 (6)	108	9.13	6.9
$(C_2B_8H_9)_2-C_2B_8H_8$	362 (22)	257	11.22	0.4
$(C_2B_8H_9)_2-C_2B_8H_8$	362 (19)	258	11.29	0.8
4,6- $C_2B_7H_{12}Cl$	150 (15) ^a	143	11.37	1.6
$C_2B_8H_{11}Cl$	160 (15) ^a	154	12.53	3.2

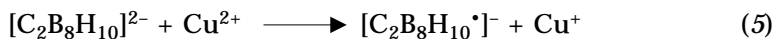
^a For the ³⁷Cl isotope.

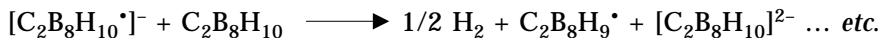
generally accepted cage-closure mechanism in the ten-vertex series¹² leads inevitably to the formation of *closo*-2,6- $C_2B_8H_{10}$ (**2**) which contains two cluster {CH} vertices in adjacent positions of high co-ordination. This highly unfavourable arrangement is then assumed to be removed by a *dsd*-type rearrangement¹³⁻¹⁵ to give a more stable carborane **3** as the main product. The presence of two other $C_2B_8H_{10}$ isomers **4** and **5**, resulting from a different alternation of the *dsd* rearrangement mode, only supports this presumption. Moreover, heating of the isomeric mixture at 350 °C leads exclusively to isomer **4** (yield 35%) with the most stable arrangement of the {CH} vertices.



SCHEME 1

The presence of several contaminant isomeric chloro derivatives $C_2B_8H_9Cl$ and of the trimeric *closo*- $C_2B_8H_9-C_2B_8H_8-C_2B_8H_9$ carboranes in the reaction mixture seems to indicate involvement of a Cu^{2+} -assisted radical-chain mechanism in the resulting reaction scheme. This may be associated with the formation of the $[C_2B_8H_{10}^{\bullet}]^-$ radical anion which may trigger several radical-chain reactions, such as, for instance, those in Eq. (5):





It may be concluded that the oxidation of the dianion **1** is a simple synthetic route and alternative access to the ten-vertex *closo*- $\text{C}_2\text{B}_8\text{H}_{10}$ carboranes **3** and **4** reported previously^{1,16-18}. Due to its simplicity, the present method also makes anion **1** a versatile source of neutral $\text{C}_2\text{B}_8\text{H}_{10}$ carboranes, in addition to its complexation properties⁵⁻⁹.

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